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SPECTRA OF PARA-BROMOBENZONITRILE

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(Plate 1)

ABSTRACT. The near ultraviolet absorption spectrum of para-bromobenzonitrile vapour has been photographed. Its infrared spectrum in the range 400 to 3000 cm^{-1} has also been recorded and the fundamentals observed in the two spectra have been assigned to corresponding modes of benzene.

INTRODUCTION

The Raman Spectrum of para-bromobenzonitrile was first photographed by Kohlrauch and Ypsilanti (1935) and the observed frequencies reported. The ultraviolet absorption spectrum of the vapour of this chemical was photographed by the author and also its infrared spectrum recorded (Pandey and Pandey, 1966). Assignments of the frequencies observed in the ultraviolet absorption spectrum have been made on the basis of comparison of their values in the Raman and infrared spectra. Wilson and Bloor's (1965) assignment of the infrared frequencies observed by them has also been compared.

EXPERIMENTAL

A pure sample of para-bromobenzonitrile was obtained from M/S Eastmen Kodak Company, New York and was used without further purification. The molecular weight of this compound is 182 and melting point 113°C. The vapour absorption spectrum in the ultraviolet was photographed on a Hilger Medium quartz spectrograph with HF_3 hydrogen arc lamp as a source of continuous radiation. Para-bromobenzonitrile vapour was obtained by introducting a small amount of this chemical in a cylindrical pyrex tube fused to two pyrex-quartz graded seals at its ends. The quartz ends of the graded seals were fused to plane quartz windows. The tube was heated by passing regulated amount of electric current through a nichrome coil wound over the entire length. The effective length of the absorption tube was one meter and with Ilford N30 photographic plates five to fifteen minutes exposures were required to photograph the longer wavelength system (Plate 1) at slit width .03 mm when the heating current was varied from .5 to 1 amp. The lower wavelength system appears at 10 cm vapour

column without any external heating. This requires an exposure of about 30 minutes.

Bands were measured on a Hilger comparator with a least count of .001 mm. The strong and sharp bands (table 1) of the longer wavelength system have an accuracy of 5 cm^{-1} but the broad and diffuse ones have hardly an accuracy of 10 cm^{-1}. The highly diffused bands of the second system have inaccuracy of higher order.

The infrared record (fig. 2) for the 400-700 cm^{-1} region was obtained from an U.R. 10 infrared spectro-photometer and for the higher frequency region a Perkin Elmer Model 137 B infrachord with NaCl optics was used. For the lower

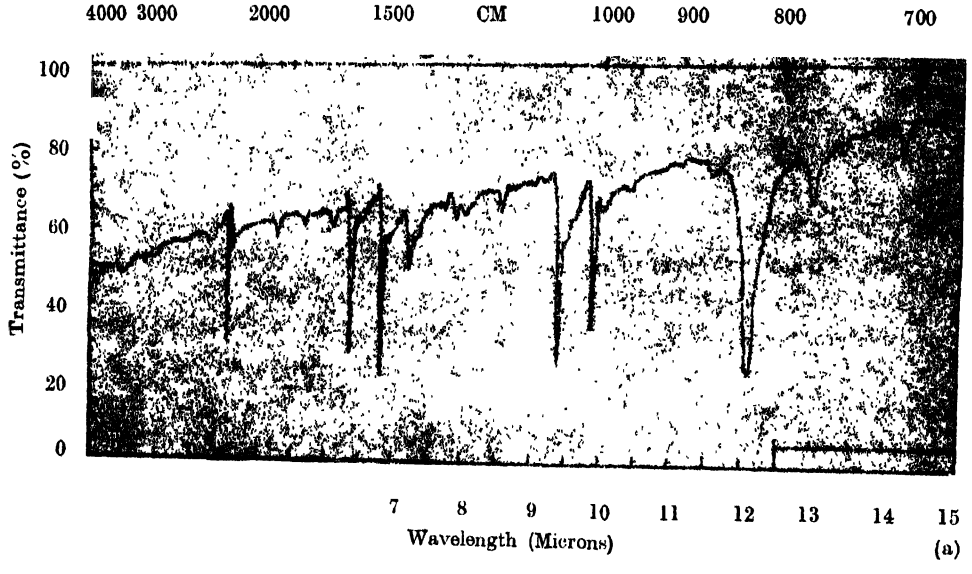

Fig. 2. Infrared spectra of parabromobenzonitrile.
(a) 700 to 3000 cm^{-1} region (KBr phase).
(b) 400 to 700 cm_{-1} region (Nujol phase).

frequency region the chemical was used in the form of fine suspension in Nujol but for the higher frequency region it was mixed with KBr to form a thin disc. Measurements of the bands (table 2) were made with the help of the scales given on the charts. They involve an accuracy of nearly 5 cm^{-1} for the 400-700 cm^{-1} region but the average accuracy in the higher frequency region is of the order of 10 to 15 cm^{-1}.

Intensities of bands in the ultraviolet absorption spectra are visual estimates. These in the infrared spectra have been shown by the difference of percentage transmittances at the peak and the back-ground at that position. As the instruments used for the two infrared regions were different, the intensities of the lower frequency region bands have been converted to correspond to the intensity condition of the higher frequency region bands. But the conditions in both the cases being different in a number of ways this conversion is approximate.

DISCUSSION

Like other parasubstituted halogen benzonitriles the parabromobenzonitrile molecule also may be taken to belong to C_{2v} point group. If the plane of this molecule be the YZ plane it should have A_1 type of ground electronic states and B_2, A_1 types of two excited electronic states corresponding to the A_{1g} (ground electronic state) and B_{2u}, B_{1u} (excited electronic states) of benzene respectively. The b_1 (type of vibrations are symmetry forbidden for both the ground state and excited state transitions in the ultraviolet spectrum corresponding to $B_2 \leftarrow A_1$ electronic transition. They are allowed, however, in the ultraviolet spectrum corresponding to the electronic transition $A_1 \leftarrow A_1$.

The longer wavelength system of bands (fig. 1) in the region 2700A of the ultraviolet absorption spectrum may correspond to the $B_2 \leftarrow A_1$ electronic transition and the shorter wavelength system in the 2400A region to the $A_1 \leftarrow A_1$ electronic transition. The 0-0 band for the first system (table 1) has been located at 36249 cm^{-1} and is shifted towards red by 1940 cm^{-1} with respect to the 0-0 band of the corresponding system of benzene (38089 cm^{-1}). The 0-0 band of the second system has been located at 41741 cm^{-1} and is shifted towards red by 5039 cm^{-1} with respect to the 0-0 band (46780 cm^{-1}) of the corresponding system of benzene. The bands in this system are rather weak and highly diffuse.

THE LONGER WAVELENGTH SYSTEM

On the longer wavelength side of the 0-0 band of the 2700A system, bands with separations 20, 42, 58, 77 and 100 cm^{-1} may be assigned to $v-v$ transitions. The 428 cm^{-1} band on this side may correspond to mode ν^*_{16a} of benzene vibration. To the shorter wavelength side of the 0-0 band there is a band with a separation

*E. B. Wilson's notations have been used.

of 227 cm^{-1}. This may correspond to the excited state value of the 428 cm^{-1} frequency. If this assignment be correct the weak 432 cm^{-1} band (table 2) in the infrared spectrum (fig. 2) may be taken to correspond to this mode of vibration. This mode being of species a_2 its intensity in the infrared spectrum is low but the double quantum transition 2×432 cm^{-1} has fairly good intensity and thus supports the present assignment. The reduction of the 428 cm^{-1} frequency to 227 cm^{-1} in the excited state leads the present assignment proposed for it to uncertainty. As an alternative the 227 cm^{-1} frequency may also be taken to correspond to the C-Br in plane bending vibration in parabromobenzonitrile. Wilson and Bloor (1965) have assigned the 432 cm^{-1} frequency, observed by them in the infrared spectrum of parabromobenzonitrile to mode ν_{12} of benzene vibrations. The intensities of the corresponding bands in this work do not favour this assignment of theirs and hence an alternative assignment has been proposed.

The other band with a separation of 501 cm^{-1} on the red side of the 0-0 band may be assigned to the totally asymmetric C-Br stretching vibration. Its weak appearance may be due to low Boltzman factor and low vapour pressure. C-Br stretching frequencies of this order of magnitude are expected to appear in the spectra of bromine substituted benzene derivatives (Brugel 1962).

The 543 cm^{-1} band on the red side of the 0-0 band may correspond to the C-CN in plane bending mode. The band with 490 cm^{-1} separation on the violet side of the 0-0 band may correspond to the excited state value of this frequency. The $v-v$ transition for it may overlap with the 58 cm^{-1} band on the red side of the 0-0 band and the infrared band at 540 cm^{-1} may be taken to correspond to this mode of vibration. Wilson and Bloor also have obtained a frequency of 543 cm^{-1} in the infrared spectrum of parabromobenzonitrile but they have assigned it to mode ν_{11} of benzene. This mode being of species b_1 should not appear in the ultraviolet absorption spectrum corresponding to the electronic transition $B_2\leftarrow A_1$ and hence the present assignment has been preferred. The non-totally symmetric component of 606 cm^{-1} benzene vibration may correspond to the 640 cm^{-1} band on the red side of the 0-0 band. It is extremely weak probably due to low Boltzman factor and low vapour pressure. A Raman frequency at 636 cm^{-1} has been reported (Kohlrausch *et al*, 1935) for parabromobenzonitrile which may correspond to the 640 cm^{-1} frequency of the ultraviolet absorption spectrum and supports the assignment proposed for it.

On the violet side of the 0-0 band, a band with a separation of 732 cm^{-1} has been taken to be a fundamental. This may be taken to correspond to the excited state value of the ring breathing frequency of parabromobenzonitrile. Its ground state value has not appeared in the ultraviolet spectrum, probably due to low Boltzman factor but the strong band at 827 cm^{-1} in the infrared spectrum may be taken to correspond to the ground state value of this frequency. Wilson and Bloor's assignment of their 824 cm^{-1} infrared frequency to mode

ν_{10b} does not explain the intensity of the 732 cm^{-1} excited state frequency and hence the present assignment has been proposed.

On the violet side of the 0-0 band another band with a separation of 1060 cm^{-1} has been taken to be fundamental. This may correspond to mode ν_{15} of benzene. In the infrared spectrum a band with frequency of 1065 cm^{-1} has good intensity expected of a fundamental. This may be taken to correspond to the 1060 cm^{-1} excited state frequency of the ultraviolet absorption spectrum. The remaining two bands on the violet side of the 0-0 band, which have been taken to be fundamentals, have separations of 1180 cm^{-1} and 1290 cm^{-1}. The first of these may be taken to correspond to mode ν_{19b} of benzene vibrations. The strong band at 1396 cm^{-1} (Wilson and Bloor's value 1405 cm^{-1}) in the infrared spectrum may be taken to correspond to the ground state value of the 1180 cm^{-1} frequency of the ultraviolet absorption spectrum. Mode ν_{8a} of benzene vibrations also should not change much for the parasubstituted benzene derivatives because it involves mainly the carbon bonds. The strong band at 1587 cm^{-1} (Wilson and Bloor's value 1589 cm^{-1}) in the infrared spectrum has been taken to correspond to this mode of vibration. The 1290 cm^{-1} band in the ultraviolet absorption spectrum may be taken to correspond to the excited state value of the 1472 cm^{-1} frequency in the infrared spectrum.

LOWER WAVELENGTH SYSTEM

In this system only two bands can be measured with some accuracy. One which is stronger has been taken to be the 0-0 band. The other with a separation of 725 cm^{-1} on the violet side of the 0-0 band may be assigned to an excited state fundamental. As observed in the short wavelength systems of parafluorobenzonitrile (to be published) and parachlorobenzonitrile (in press) this may correspond to mode ν_1 of benzene vibrations. Its value does not change much in the second excited electronic state $^1A_1$ as has been observed in the case of the above mentioned two molecules.

In the infrared spectrum the bands which have been taken to be fundamentals and have not been discussed so far are at 773, 1011, 1175, 1275, 1472 and 2212 cm^{-1}. They should correspond to different vibrational modes of parabromobenzonitrile. The 773 cm^{-1} frequency has been assigned to mode ν_{10a} of benzene vibrations. A Raman frequency with separation of 773 cm^{-1} has been reported for parabromobenzonitrile and supports the assignment of fundamental to this frequency. Wilson and Bloor also have obtained a frequency of 772 cm^{-1} but they have left it unassigned.

Mode ν_{9a} is not much affected by substitution and hence the 1176 cm^{-1} frequency may be taken to correspond to it. This frequency may be preferably assigned to the C-CN stretching mode in parabromobenzonitrile. Similarly, the 1011 cm^{-1} frequency may be assigned to correspond to mode ν_{12} of benzene vibrations. Wilson and Bloor have assigned their 1016 cm^{-1} frequency to mode ν_{18a} but

from comparison (Padhey *et al*. 1959, 1960) this frequency appears to be almost independent of substitution and hence the present assignment has been proposed. It has been shown (Scherer 1965) that in substituted benzene the magnitude of the frequency corresponding to mode ν_{12} decreases and that of the frequency corresponding to mode ν_1 increases due to CH and CC interactions. This kind of change has not been accepted in this work, because the reduction of ν_1 with the increase in mass of the substituents is more reasonable. The 1275 cm^{-1} frequency has been assigned to correspond to mode ν_3 of benzene vibrations. Wilson and Bloor also have assigned their 1283 cm^{-1} frequency to this mode.

Table 1

Ultraviolet absorption spectrum of parabromobenzonitrile vapour

Ist. system

Band intensity	Wave number (vac) cm^{-1}	Separation from 0-0 band	Assignment
vvw	35609	640	0 – 640
vvw	35650	599	0 – 543 – 58
vvw	35679	570	0 – 543 - 20
vw	35706	543	0 – 543
vvw	35725	524	0 – 501 – 20
vw	35748	501	0 – 501
vw	35821	428	0 – 428
vvw	36149	100	0 – 100, 0 – 77 – 20
vvw	36172	77	0 – 4 × 20
vw	36191	58	0 – 58, 0 – 3 × 20
vw	36207	42	0 – 42, 0 – 2 × 20
mw	36229	20	0 – 20
ms	36249	0	0 – 0
vvw	36443	194	0 + 732 – 543
vvw	36462	213	0 + 227 – 20
vw	36476	227	0 + 227
vw	36739	490	0 + 490
vvw	36959	710	0 + 732 - 20
vw	39981	732	0 + 732
vvw	37279	1030	0 + 1060 – 20
vw	37309	1060	0 + 1060
vw	37429	1180	0 + 1180
vvw	37524	1275	0 + 1290 – 20
vw	37539	1290	0 + 1290
vvw	38014	1765	0 + 1290 + 490
wd	41741	0	0 – 0
vwd	42466	725	0 + 725

s = strong, v = very, m = medium, w = weak,
b = broad, d = diffuse.

Table 2
Infrared absorption spectrum of parabromobenzonitrile

Band intensity	Wave number cm^{-1}	Assignment
8*	432	432
32*	540	540
9	704	1472−773
12	773	773
5	827	827
5	868	2×432
5	980	432+540
40	1011	1011
12	1042	1472−432
50	1065	1065
2	1089	2×540
10	1175	1175
7	1254	827+432
8	1275	1275
5	1306	773+540
12	1344	2212−2×432
20	1396	1396
50	1472	1472
8	1540	2×773
10	1555	1011+540
45	1587	1587
5	1610	1065+540
6	1768	2212−432
2	1869	1042+827
6	1908	1472+432
35	2212	2212
3	2276	1275+1011
3	2330	1275+1065
5	2352	2×1175
3	2865	1472+1396
3	3039	3039
		2212+827
3	3344	1472+1065+827

* Converted intensities

Table 3

Correlation and mode assignment of the frequencies observed in the spectra of para-bromobenzonitrile

Raman cm^{-1}	Infrared		Ultraviolet		Assignment	Mode
	This work cm^{-1}	Wilson etc. cm^{-1}	G.S. cm^{-1}	E.S. cm^{-1}		
421	432	432	428	227	δ(C—C)a_2	16a (12)
—	—	—	501	—	ν(C—Br)a_1	—
533	540	543	543	490	β(C—CN)b_2	(11)
636	—	—	640	—	β(C—C)b_2	6b
765	773	772	—	—	δ(C—H)a_2	10a
—	827	824	—	732	ν(C—C)a_1	1 (10b)
—	1011	1016	—	—	β(C—C)a_1	12 (18a)
1064	1065	1071	—	1060	β(C—H)b_2	15
1179	1175	1177	—	—	β(C—H)b_2 + ν(C—CN)a_1	9a
—	1275	1283	—	—	β(C—H)b_2	3
—	1396	1405	—	1180	ν(C—C)b_2	19b
—	1472	1485	—	1290	ν(C—C)a_1	19a
1582	1587	1589	—	—	ν(C—C)a_1	8a
2229	2212	2230	—	—	ν(C≡N)a_1	

(ν = stretching, β = in place bending, δ = out of plane bending. Modes in perentheses are those proposed by Wilson *et al*, 1965).

The band at 1344 cm^{-1} in the infrared spectrum has intensity expected of a fundamental but fundamentals with frequencies of this order of magnitude are not expected for parabromobenzonitrile type of molecules. As such this band has been explained as a difference band. It has been shown to arise due to the difference of 2212 cm^{-1} frequency and the 2×432 cm^{-1} transition but this assignment is not favourable to the observed intensity. The alternative to this will be the assumption that this band might have appeared due to combination of some lower vibrational frequency with some higher one having value below 1344 cm^{-1}.

The 1472 cm^{-1} (Wilson and Bloor's value 1485 cm^{-1}) frequency have been taken to correspond to mode ν_{19a} of benzene vibrations. This mode has appeared with frequency 1481 cm^{-1} in the infrared spectrum of parachlorobenzonitrile and

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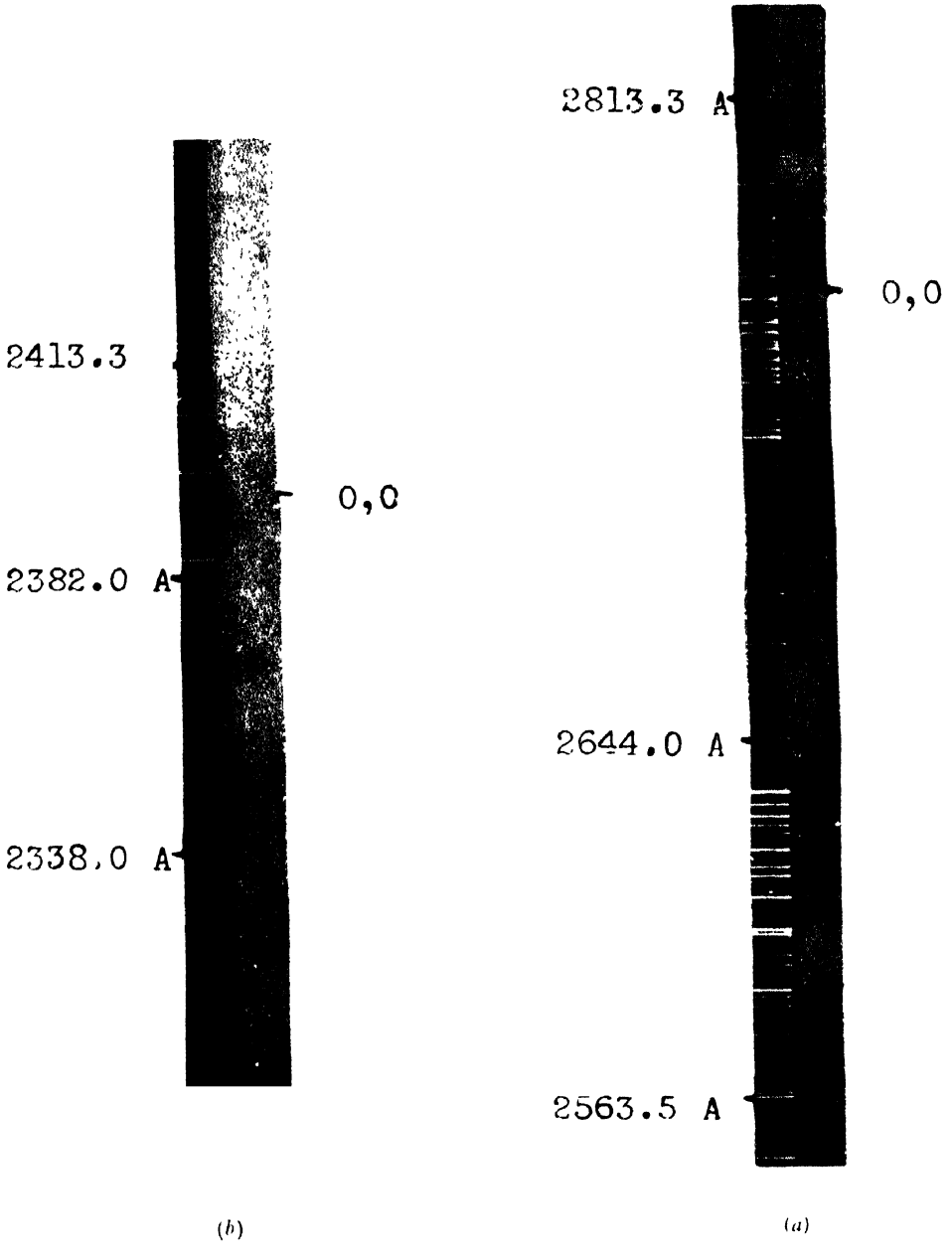

Fig 1. Ultraviolet absorption spectra of parabromobenzonitrile vapour
(a) Longer wavelength system.
(b) Shorter wavelength system.

1506 cm^{-1} in the infrared spectrum of parafluorobenzonitrile. These values support the assignment proposed here for this mode in parabromobenzonitrile.

As in other CN substituted molecules we should expect in the infrared spectrum of parabromobenzonitrile a frequency of the order of 2200 cm^{-1} representing the CN stretching vibration. The 2212 cm^{-1} (Wilson and Bloor's value 2230 cm^{-1}) frequency has been assigned to this mode in parabromobenzonitrile. In the Raman spectrum (Kohlrausch *et al*, 1935) of this molecule a frequency of 2229 cm^{-1} has been reported which has been taken to correspond to the 2212 cm^{-1} frequency of the infrared spectrum. The slightly higher value of the Raman frequency may be partly due to phase change or this may be partly because of the limit of accuracy in measurement.

Wilson and Bloor have assigned the infrared frequencies 1304 cm^{-1}, 701 cm^{-1}, 980 cm^{-1} and 866 cm^{-1} to modes ν_{14}, ν_4, ν_5 and ν_{10a} of benzene vibrations. These frequencies have been obtained also by the author (respective values are 1306 cm^{-1}, 704 cm^{-1}, 980 cm^{-1} and 862 cm^{-1}) but these have been explained to arise due to combination of the frequencies already discussed. Wilson and Bloor have left the 1071 and 772 cm^{-1} frequencies unassigned but these (present value 1065 and 773 cm^{-1} respectively) have been assigned to mode ν_{15} and ν_{10a} respectively. Also the 1258 cm^{-1} and 1093 cm^{-1} frequencies left unassigned by them have been explained by the author as combination frequencies.

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